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Investigations of Vermiculite and Other Samples from the Libby, Montana Region

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Introduction The following is a viewgraph presentation shown at the Interactive Asbestos Meeting, April 25-26, 2000 at the Denver Federal Center. The meeting was to provide a forum for EPA regions and Program Offices, other Federal agencies, States and others to discuss risk assessment and analytic issues related to tremolite-actinolite series asbestos fibers with focus on fibers from the Libby, Montana ore body. This meeting was an EPA lead meeting, hosted at USGS facilities.

The report here shows results of research funded by the EPA to the USGS to study the mineralogic properties of the Libby, Montana ore body and processed material. USGS Director's Approval: June 30, 2000.

What we know so far

Mineralogy:

- "Vermiculite" ore contains at least 3 phases:
 - Vermiculite
 - Hydrobiotite (mixed layer vermiculite-biotite)
 - Biotite
 - Hereafter referred to simply as "vermiculite"
 - The "tremolite" associated with the ore has been
 - Referred to as Na-tremolite. Modern mineralogical
 - Classification is richterite
 - (See Deer, Howie, Zussman, 1965)
-

Electrostatic Charge:

- All minerals observed display different levels of electrostatic

charge.

- Each vermiculite, hydrobiotite, or biotite flake has shown some electrostatic charge, some more than others. Biotite shows the least charge, vermiculite the most.
 - Ultrasonically washed flakes also show charge.
 - Richterite grains show significant charge.
 - Richterite, electrostatically clinging to "vermiculite"
 - Grains apparently neutralize the **NET** charge.
 - Richterite grains have been observed to electrostaticly jump to and/or cling to:
 - Rubber
 - Glass
 - Porcelain
 - Aluminum
 - Libby "vermiculite" ore
 - **Analogies:**
 - "The richterite grains appear like iron filings with everything being a magnet."
-



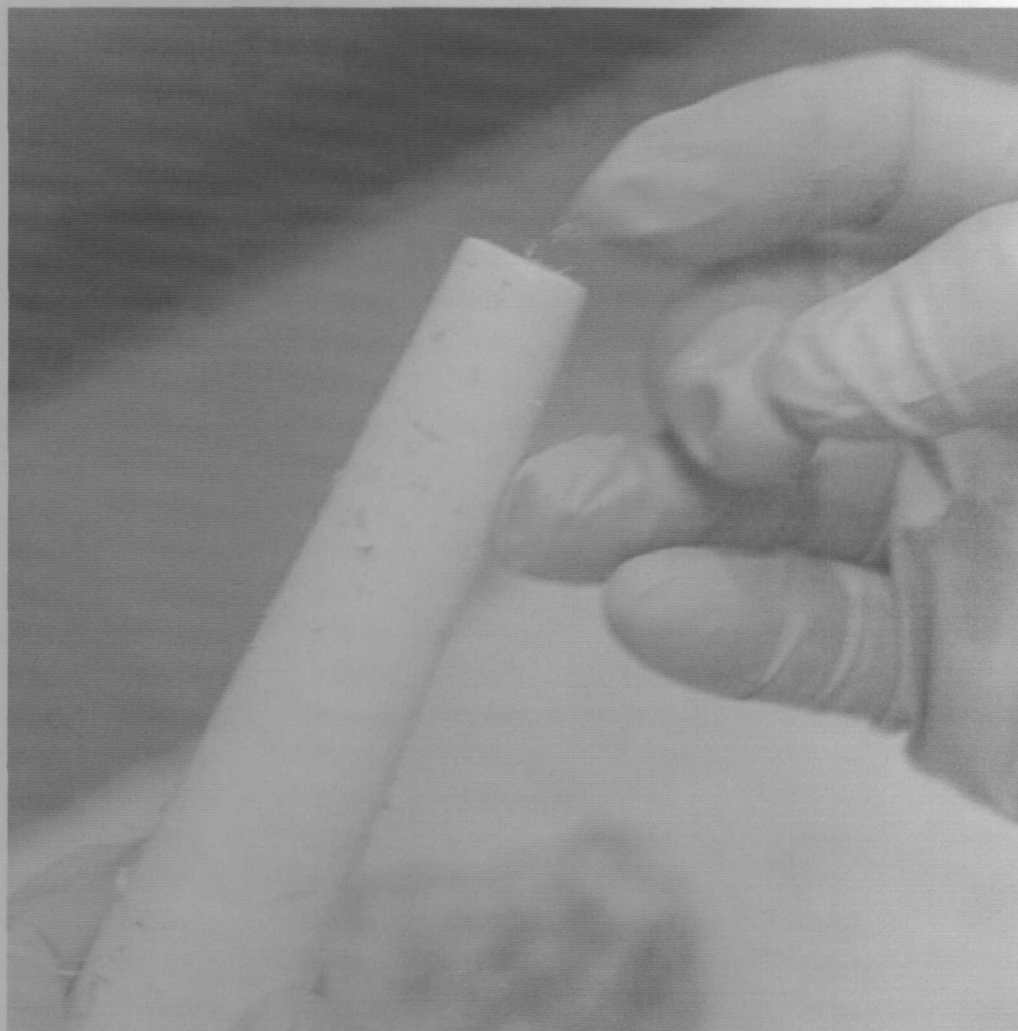
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Figure 1: Richterite grains from the Libby, MT area show electrostatic charge. Here grains electrostatically cling to a ceramic pestle and are attracted to a rubber glove.



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Figure 2: Richterite grains cling to the ceramic mortar as they are poured from the container.



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Figure 3: Richterite grains from the Libby, MT jump from the ceramic pestle to a rubber glove due to electrostatic charge.

A set of standards has been prepared

- Samples from Libby area
- **Richterite** rock (mostly pure, fibrous richterite, trace quartz,

- corundum)
 - **Vermiculite ore:**
 - Ultrasonically washed 19 times:
 - 14 times in water
 - 5 times in isopropyl alcohol
 - Samples:
 - ore + 0.1 wt % richterite
 - ore + 0.2 wt % richterite
 - ore + 0.5 wt % richterite
 - ore + 1.0 wt % richterite
 - ore + 2.0 wt % richterite
 - ore + 5.0 wt % richterite
 - Standards studied with:
 - X-Ray Diffraction (XRD),
 - Near-IR reflectance spectroscopy,
 - Scanning Electron Microscopy (SEM),
 - Energy Dispersive X-Ray Spectroscopy (EDS),
 - Electron Microprobe (EPMA), and
 - X-Ray Fluorescence (XRF).
-

The Libby, MT Amphibole:

- XRF, XRD, EPMA, EDS confirmed amphibole composition near richterite.
- XRD has found multiple phases, including:
 - Vermiculite
 - Hydrobiotite (mixed layer vermiculite - biotite)
 - Biotite
 - Richterite
- XRD has good detection limits
- XRD Requires sample preparation.

- XRD acquisition: ~hour (longer for lower detection limits)

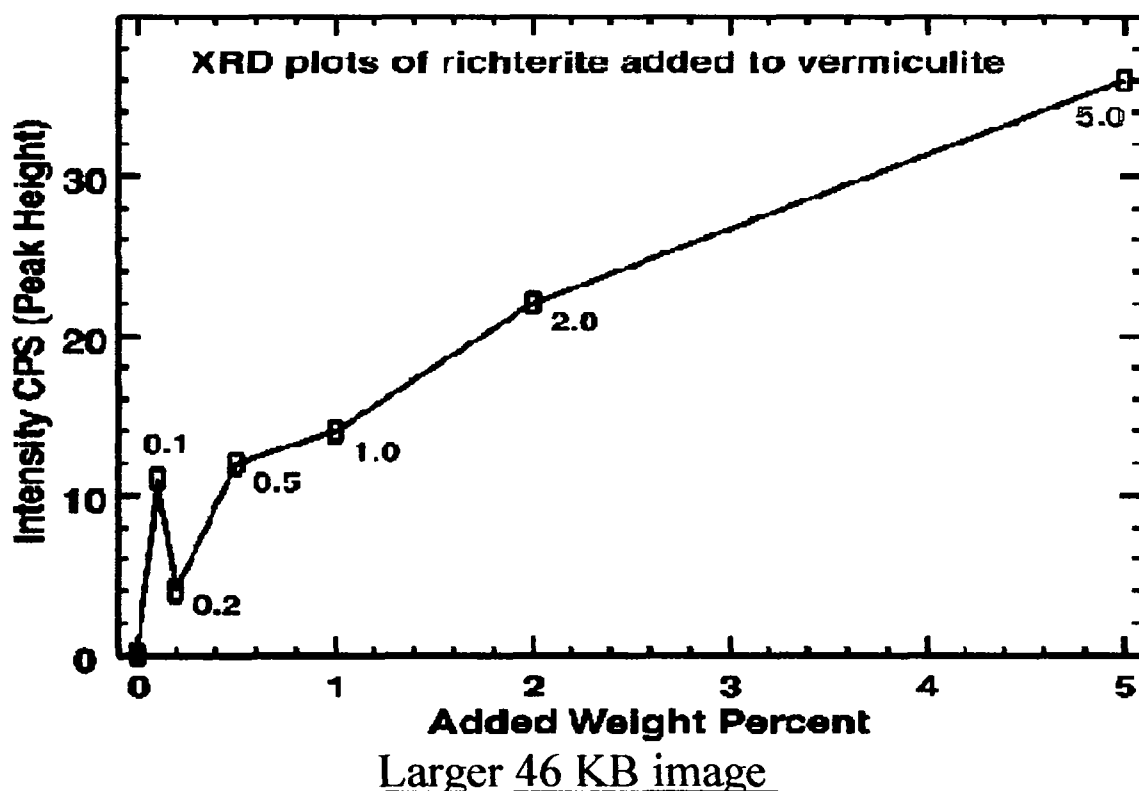
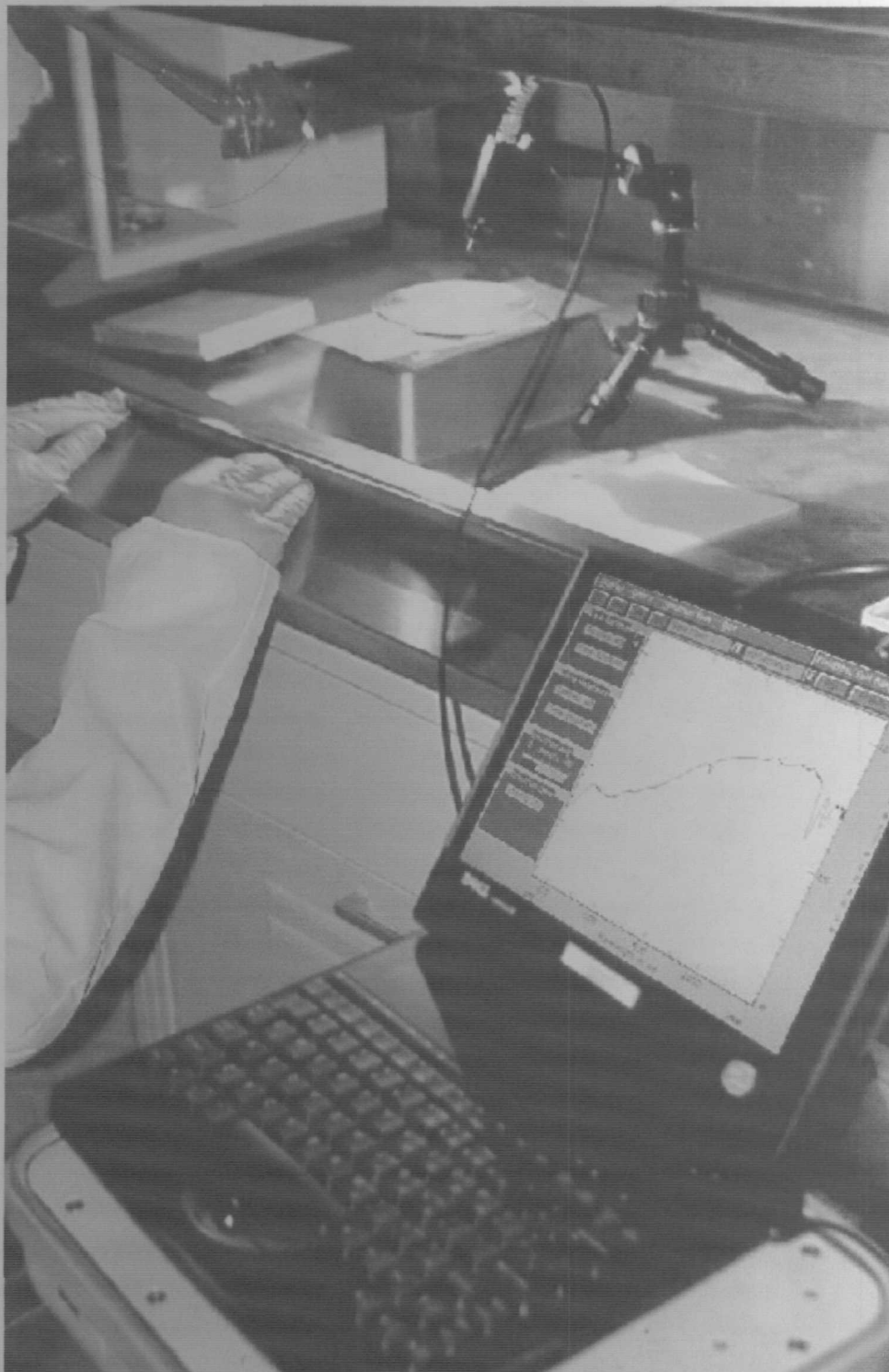


Figure 4. XRD peak height for constructed Libby vermiculite + richterite mixtures. The error bar in the measurement is approximately the size of the small rectangles. The large variation in the trend at low added weight percent richterite is due to the residual richterite in the vermiculite. Higher concentrations of richterite in the sample masks the variability in the cleaned vermiculite flakes.

Reflectance Spectroscopy:

- Pros:
 - Probes a larger volume of material.
 - Is non-destructive.
 - No sample preparation necessary
 - Laboratory to field to detection from aircraft
 - Can obtain spectra in seconds or less on samples from millimeters to meters.
 - Good low level detection limits.
 - Cons:
 - Not quantitative (or only semi-quantitative)
 - May not be able to distinguish between fibrous versus non-fibrous richterite. (research on this topic still to be done.)
 - Considerable variability has been observed in **near-infrared spectra** of Libby vermiculite samples:
 - Ore varies between vermiculite, hydrobiotite, and biotite with variable amounts of richterite from grain to grain (from spectroscopy and XRD).
 - Even among one mineral, like vermiculite grains, the richterite content varies from grain to grain.
 - The ultrasonically washed (19 times) ore sample still contains richterite based on the presence of spectral features as well as SEM and XRD detections.
-



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Figure 5. Samples were measured in a heppa-filter equipped hood with a portable spectrometer (foreground). A fiber-optic probe goes into the hood so the equipment is outside the hood

environment. A spectrum can be obtained every few seconds. The spectrum on the screen is Libby richterite (spectrum shown in Figure 9).

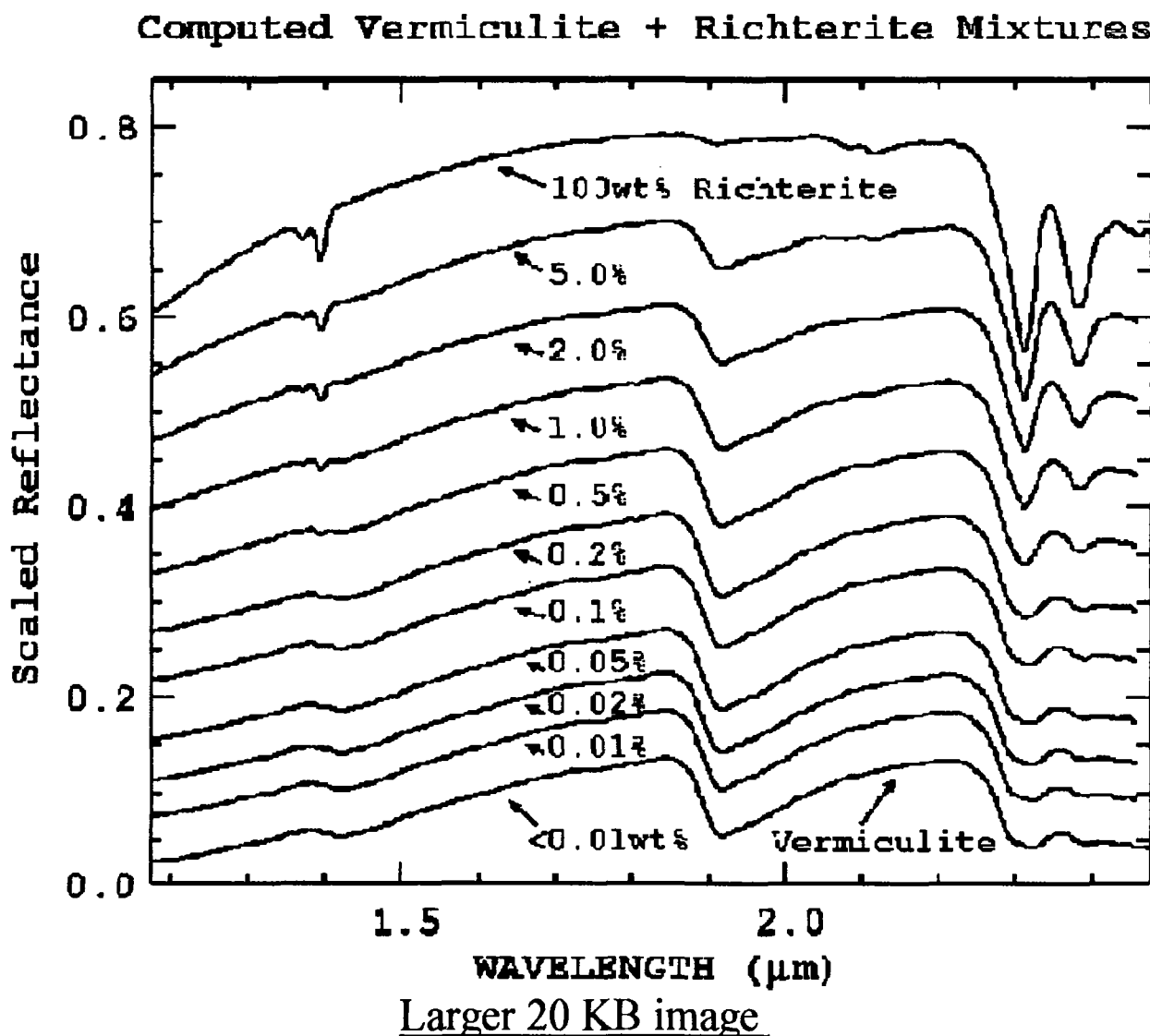


Figure 6. From the derived optical properties of Libby vermiculite and richterite, a series of spectra were computed to illustrate the expected trends in spectra of richterite - vermiculite mixtures. A richterite grain diameter of 0.5 microns on centimeter-size vermiculite flakes was used for these calculations. Richterite

shows strong absorption features at 1.393, 2.31 and 2.39 microns.
The absorption feature strengths for other grain sizes would be different from those shown here.

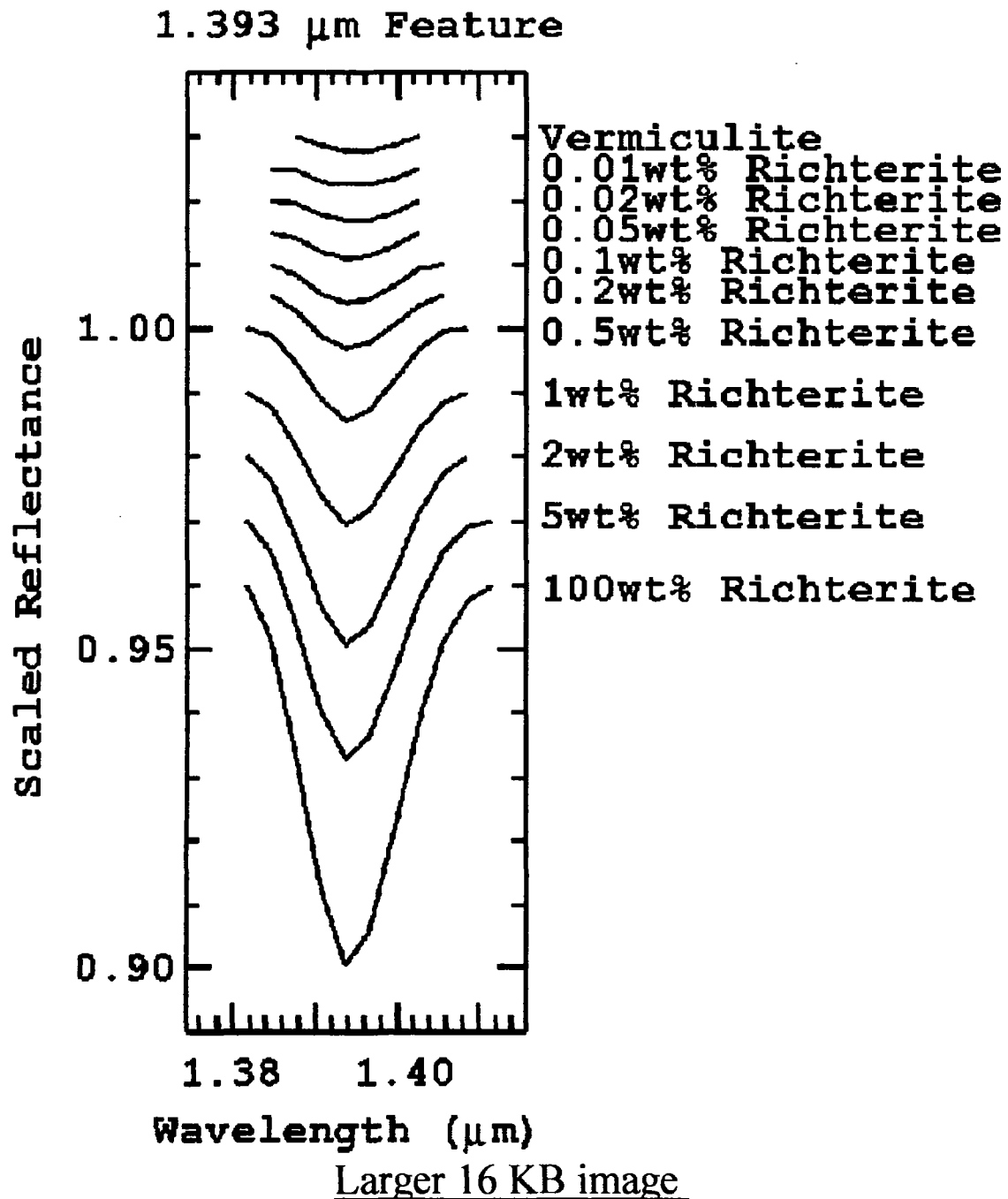


Figure 7. The feature strengths for the 1.393-micron richterite

absorption are shown from the modeled spectra in Figure 6. The residual feature in the vermiculite spectrum (top spectrum) is probably indicative of trace richterite in the vermiculite sample from which the optical properties were derived, even after the vermiculite was ultrasonically washed 19 times.

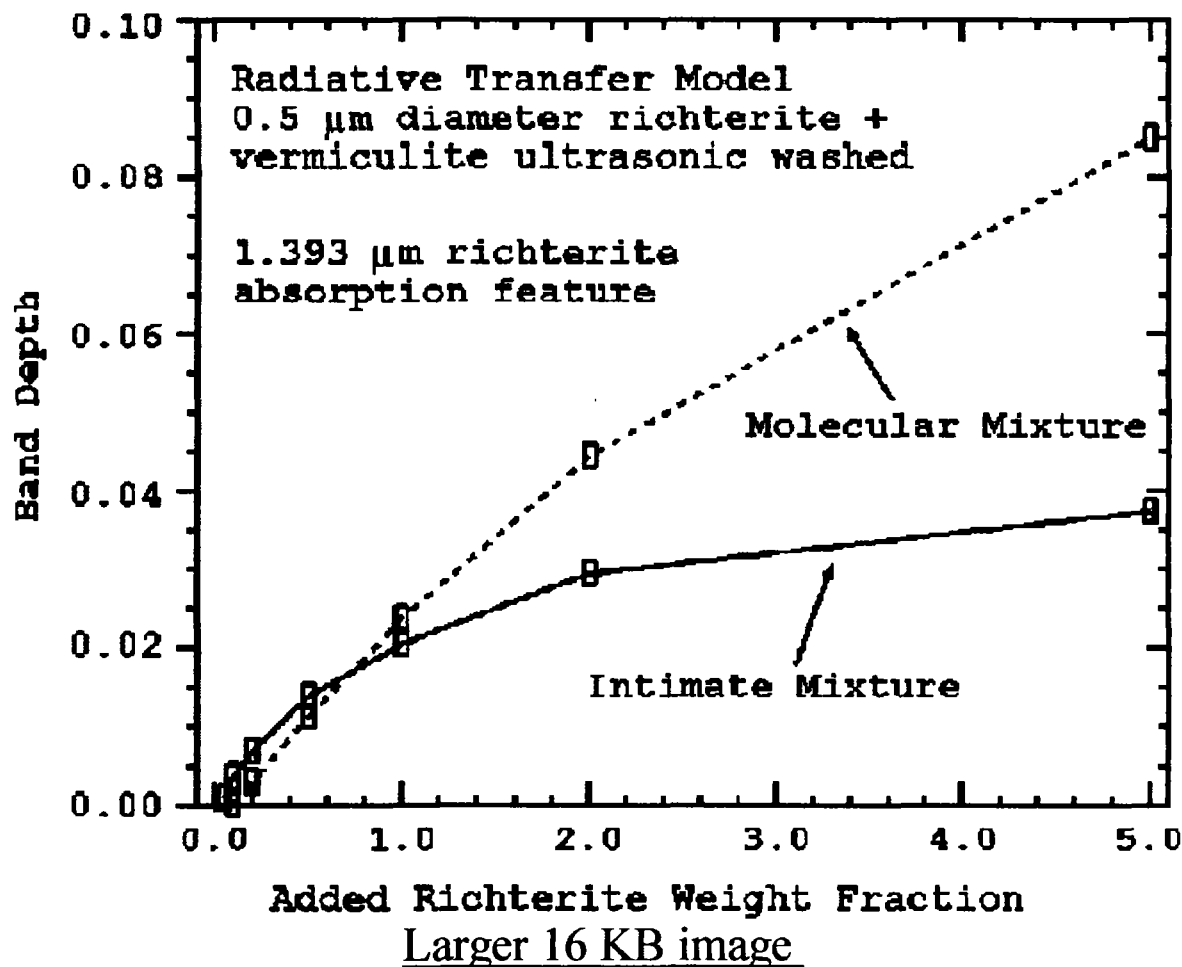


Figure 8. The 1.393-micron richterite feature strength model for intimate mixture (from Figure 7) and for richterite embedded in the vermiculite flakes is shown. Different grain-size distributions will change the magnitude of the feature strengths but the overall trends will be similar.

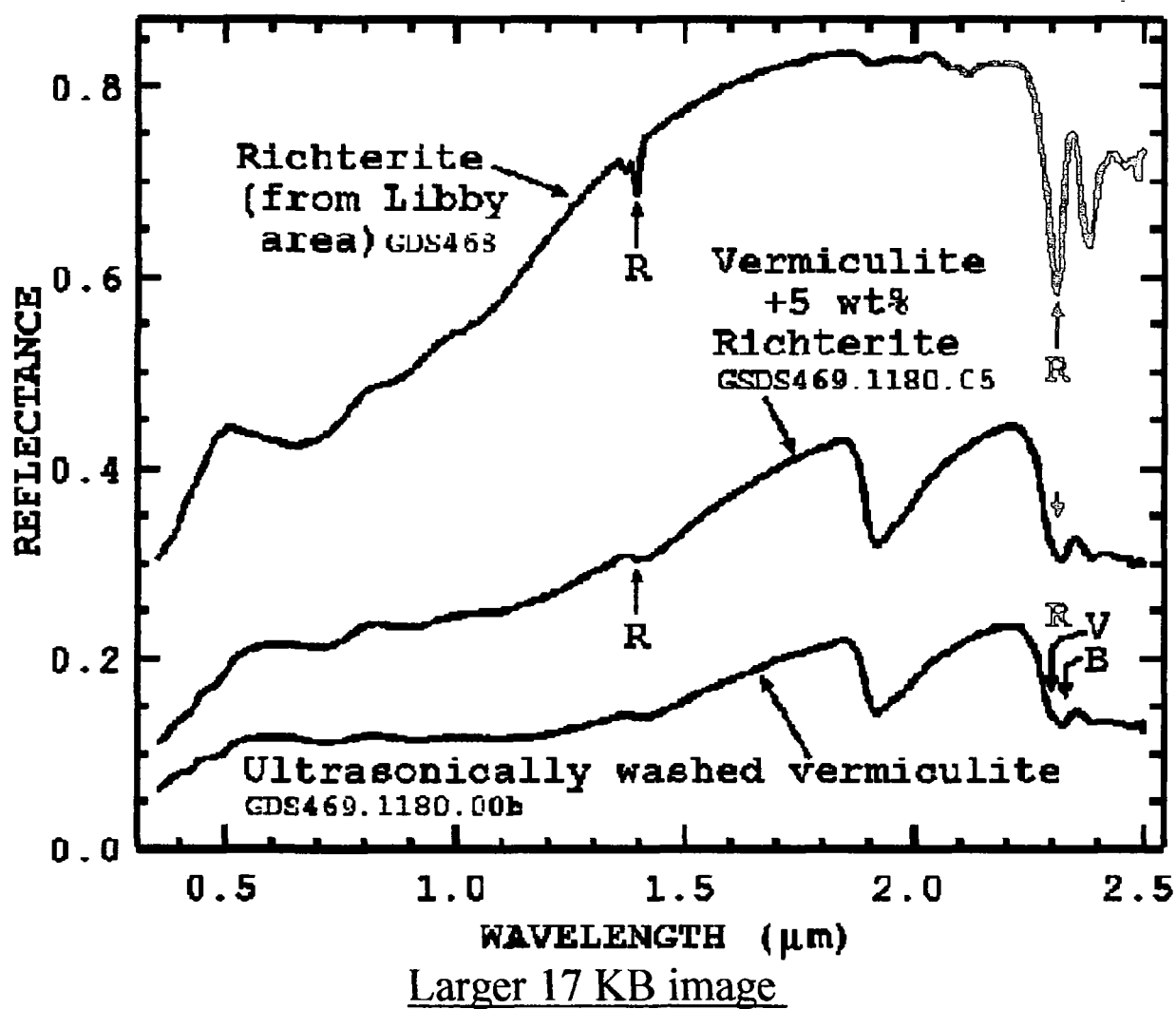


Figure 9. Measured spectra of real samples: Libby richterite (top), Libby vermiculite, washed 19 time in ultrasonic baths (bottom), and a constructed mixture of washed vermiculite and richterite (middle). The letter "R" points to richterite absorptions, "V" to vermiculite absorption, and "B" to biotite absorption.

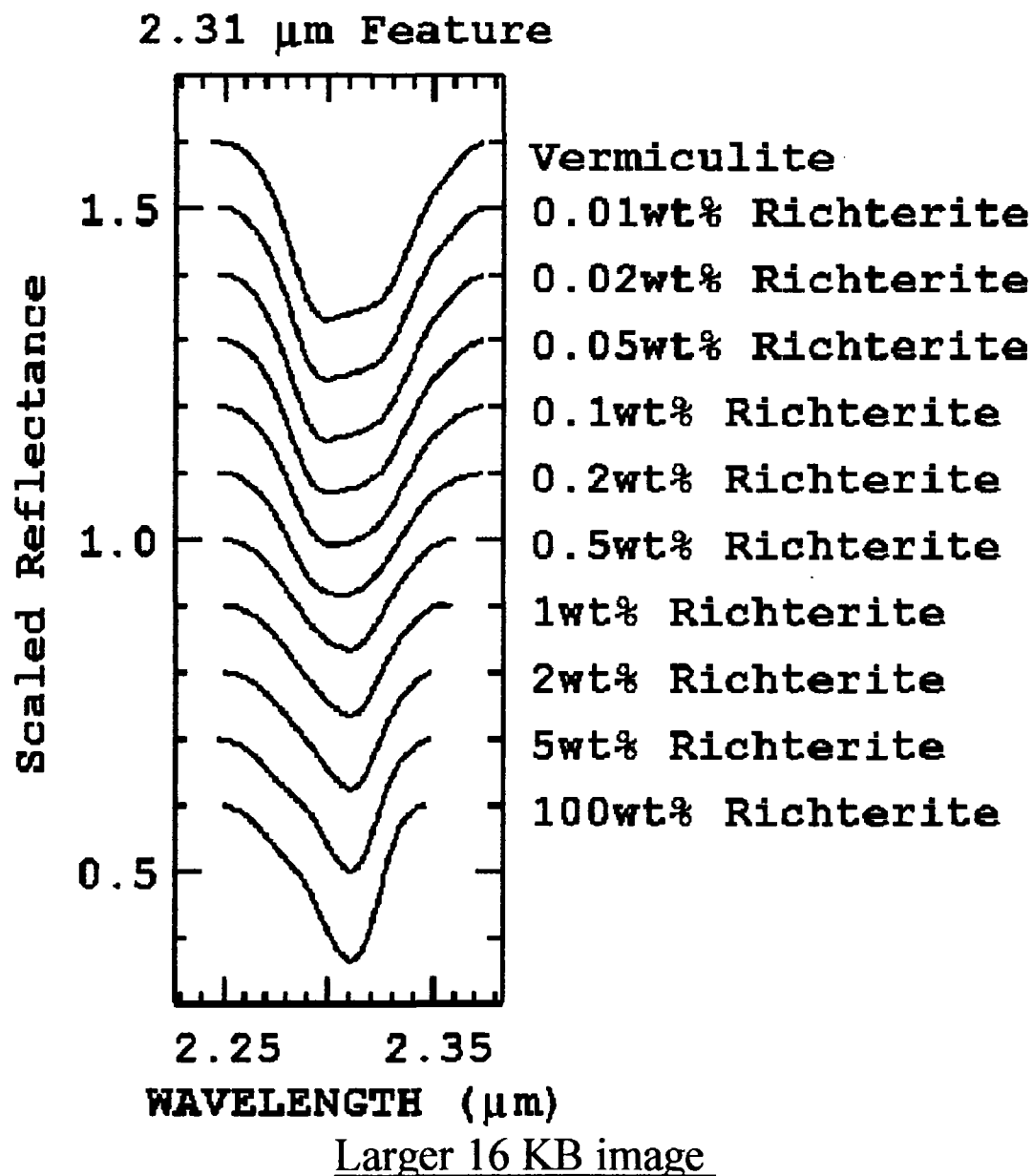
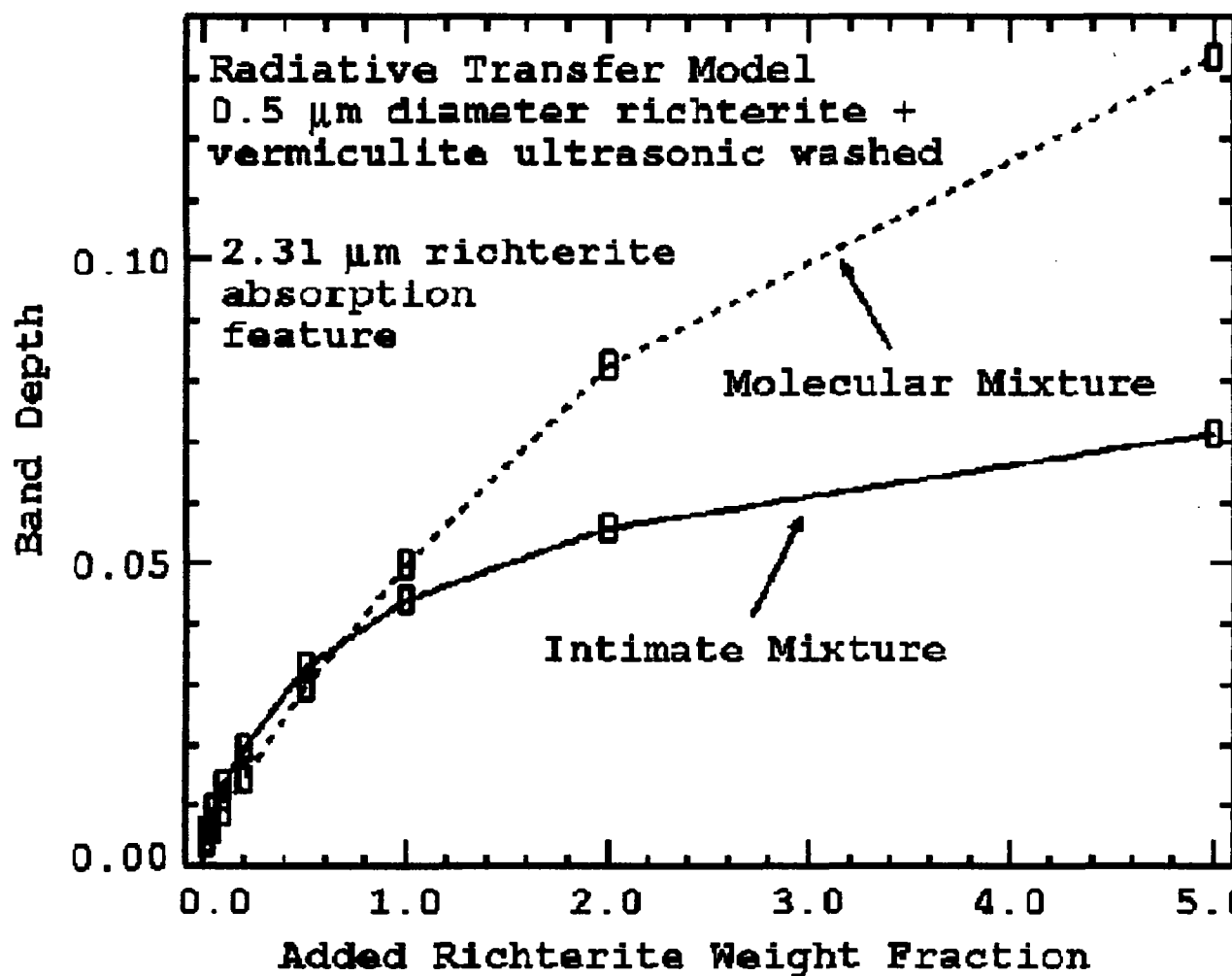
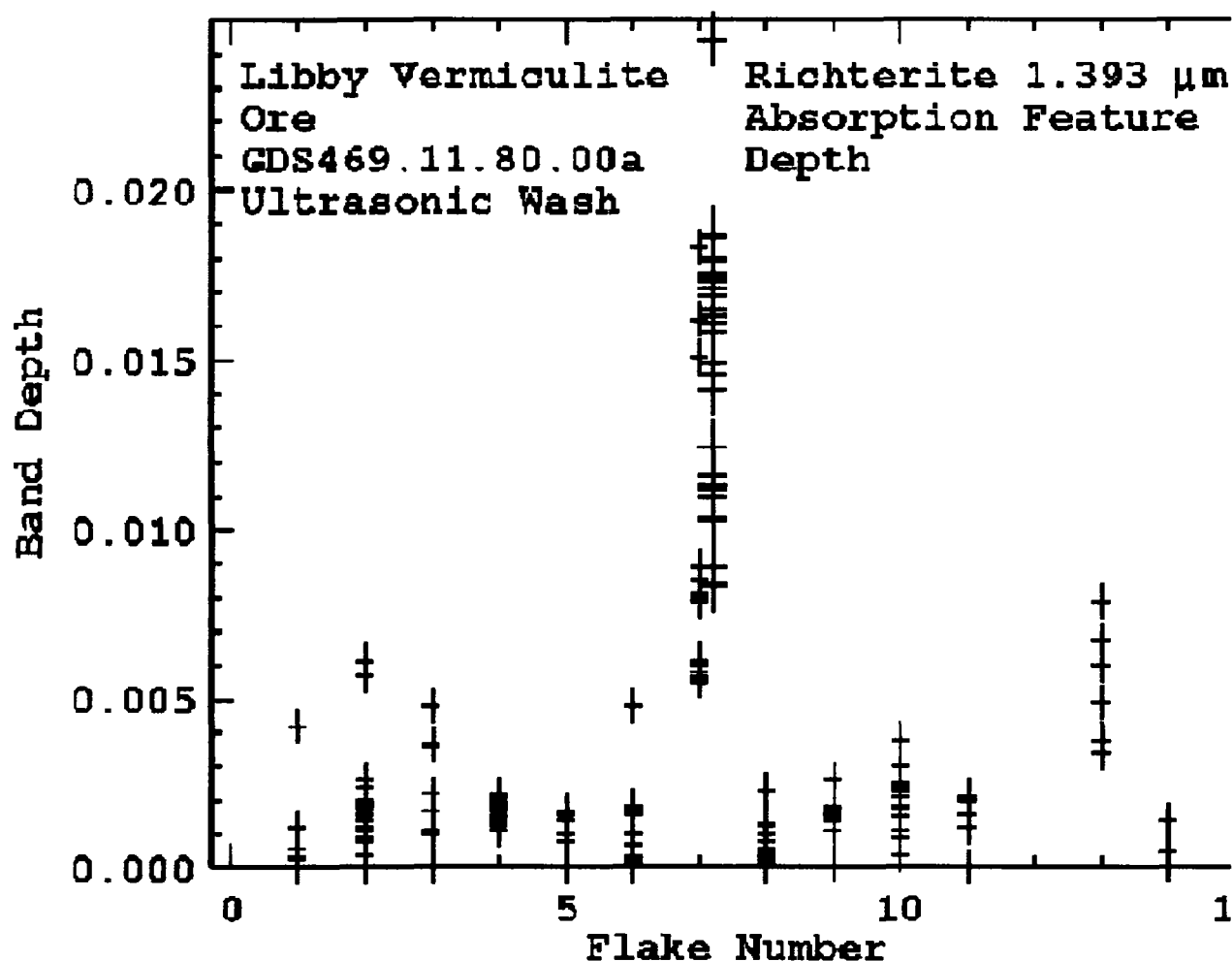


Figure 10. The feature strengths for the 2.31-micron richterite absorption are shown from the modeled spectra in Figure 6.



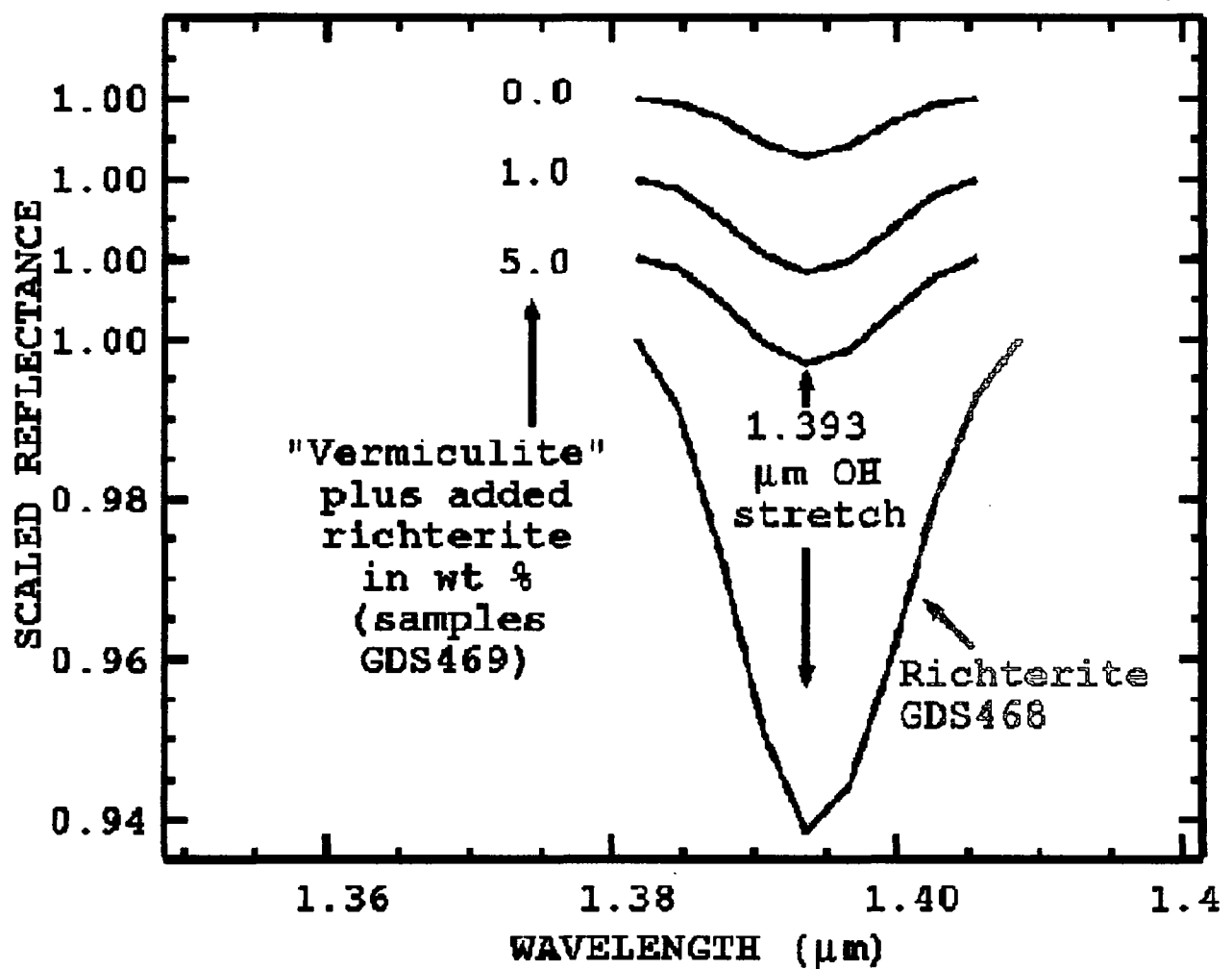
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Figure 11. The 2.31-micron richterite feature strength model for intimate mixture (from Figure 10) and for richterite embedded in the vermiculite flakes is shown. Different grain size distributions will change the magnitude of the feature strengths but the overall trends will be similar.



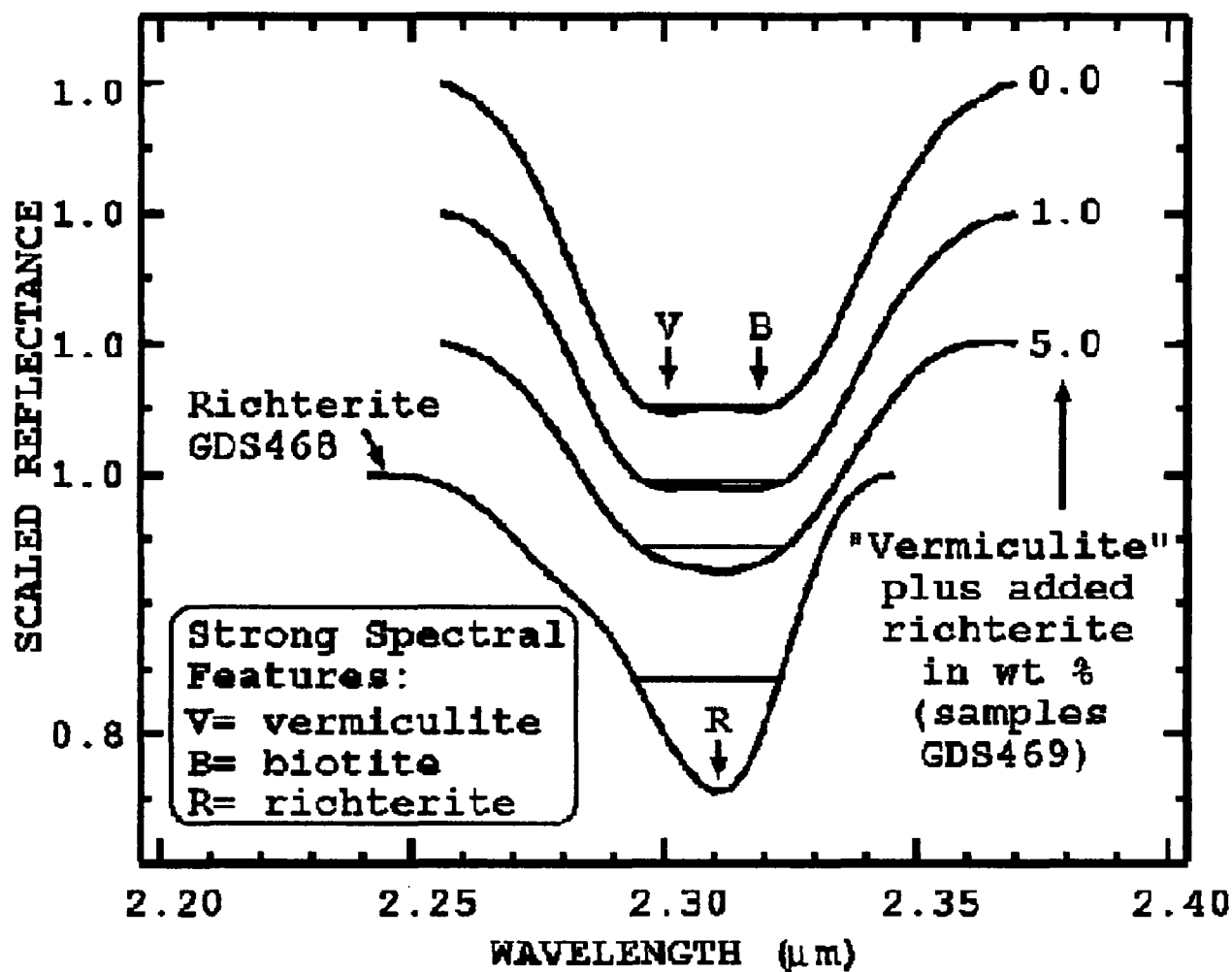
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Figure 12. Measured spectra of individual Libby vermiculite flakes are shown for the 1.393-micron richterite absorption feature. The vermiculite was washed in ultrasonic baths 19 times, yet these measurements show certain grains still contain richterite. Flake 7 showed the highest spectral indication of richterite, so the flake was split with a new, cleaned razor blade and individual pieces measured. One of those pieces (the second set of measurements to the right of the "7" line on the plot) showed very high spectral indications of richterite. This piece showed many microscopic vein-like structures in the flake through a stereo microscope. SEM images of these flake are shown in figures 20-22, and show richterite fibers.



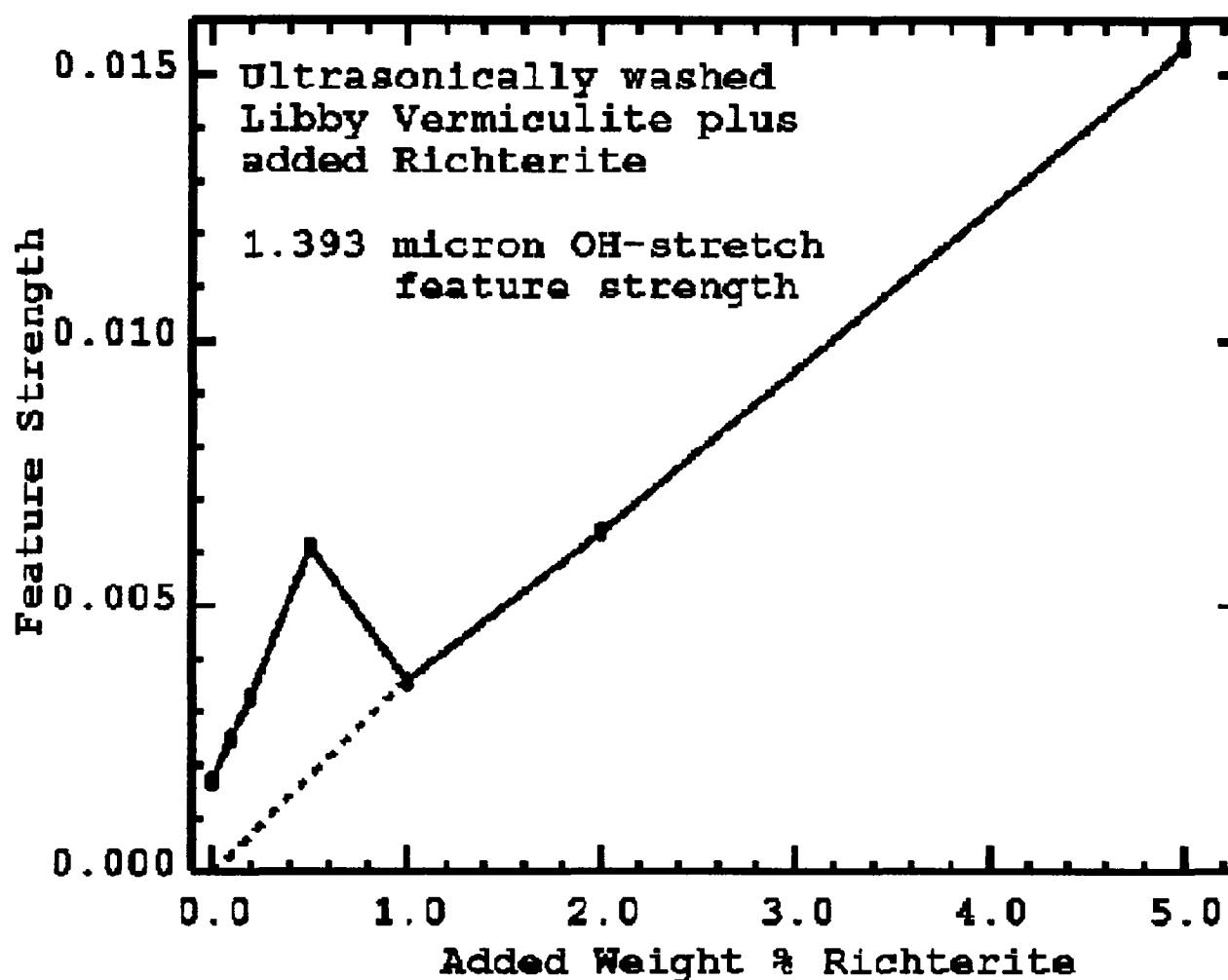
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Figure 13. Measured 1.393-micron richterite absorption strength is shown for constructed mixtures of richterite and the ultrasonically washed vermiculite. The ultrasonically washed vermiculite still shows a 1.393-micron feature. This feature may indicate residual richterite in the vermiculite--further study needs to be done.



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Figure 14. Same spectra as in figure 13, but showing the 2.31-micron feature. This feature is a combination of 3 sources: vermiculite (v), biotite (b), and richterite (r). The richterite indicator changes the curvature of the combined absorption feature.



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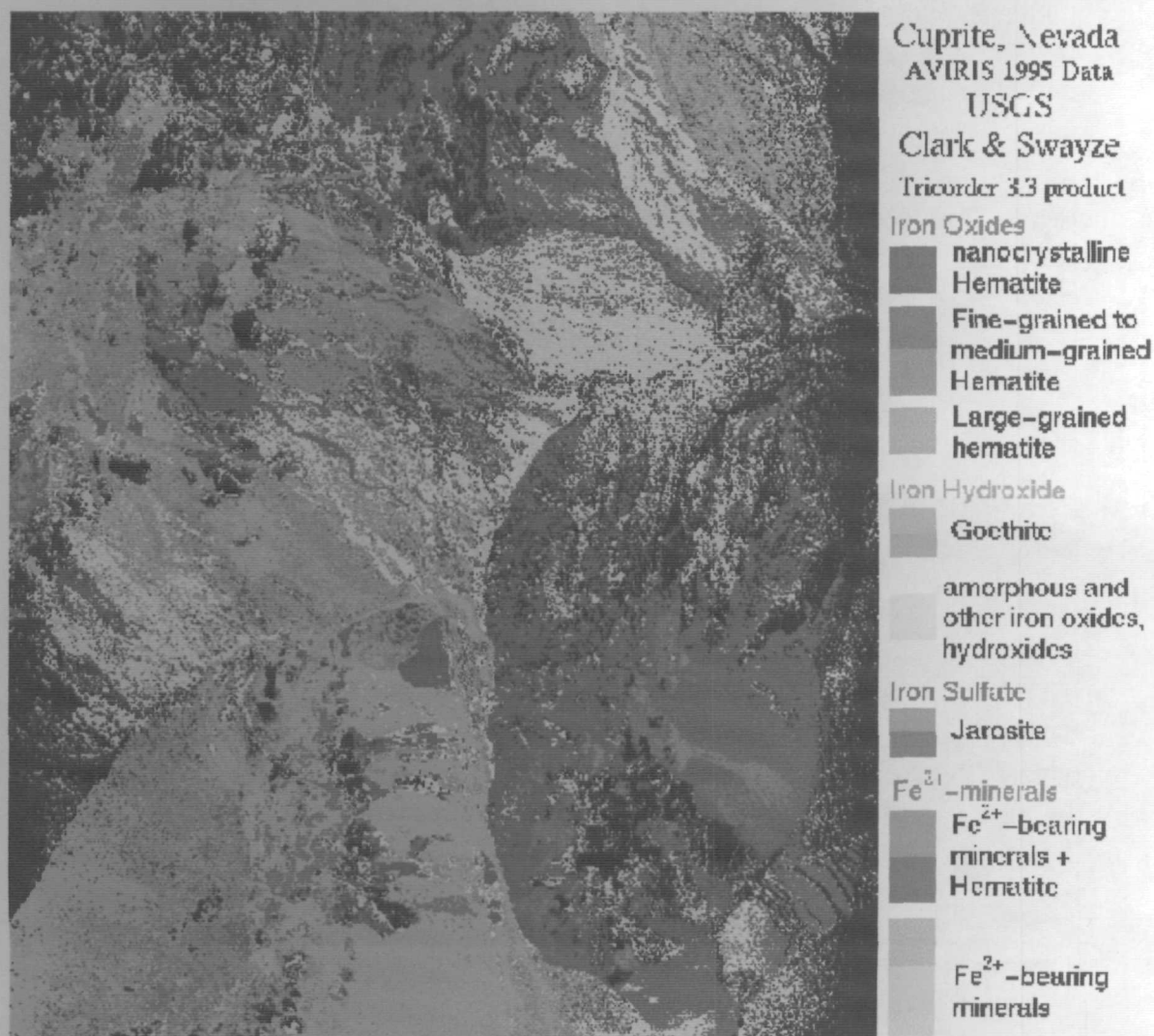
Figure 15. The measured 1.393-micron feature strength from the combined mixtures. The error bar in determining the feature strength is approximately the size of the points. The deviation from the trend line (dashed line) is due to residual richterite in the ultrasonically washed vermiculite. Compare with the observed XRD results in Figure 4. For higher concentrations of richterite in the sample, the richterite coats the vermiculite grains and thus hides the residual richterite in/on the washed vermiculite flakes, so the variability is masked. This spectroscopic result, the individual flake results in Figure 12, the XRD results, and the observed electrostatic properties indicates the richterite is highly variable and cannot easily be cleaned from the vermiculite.

Color Chart(s)

The following pages contain color that does not appear in the scanned images.

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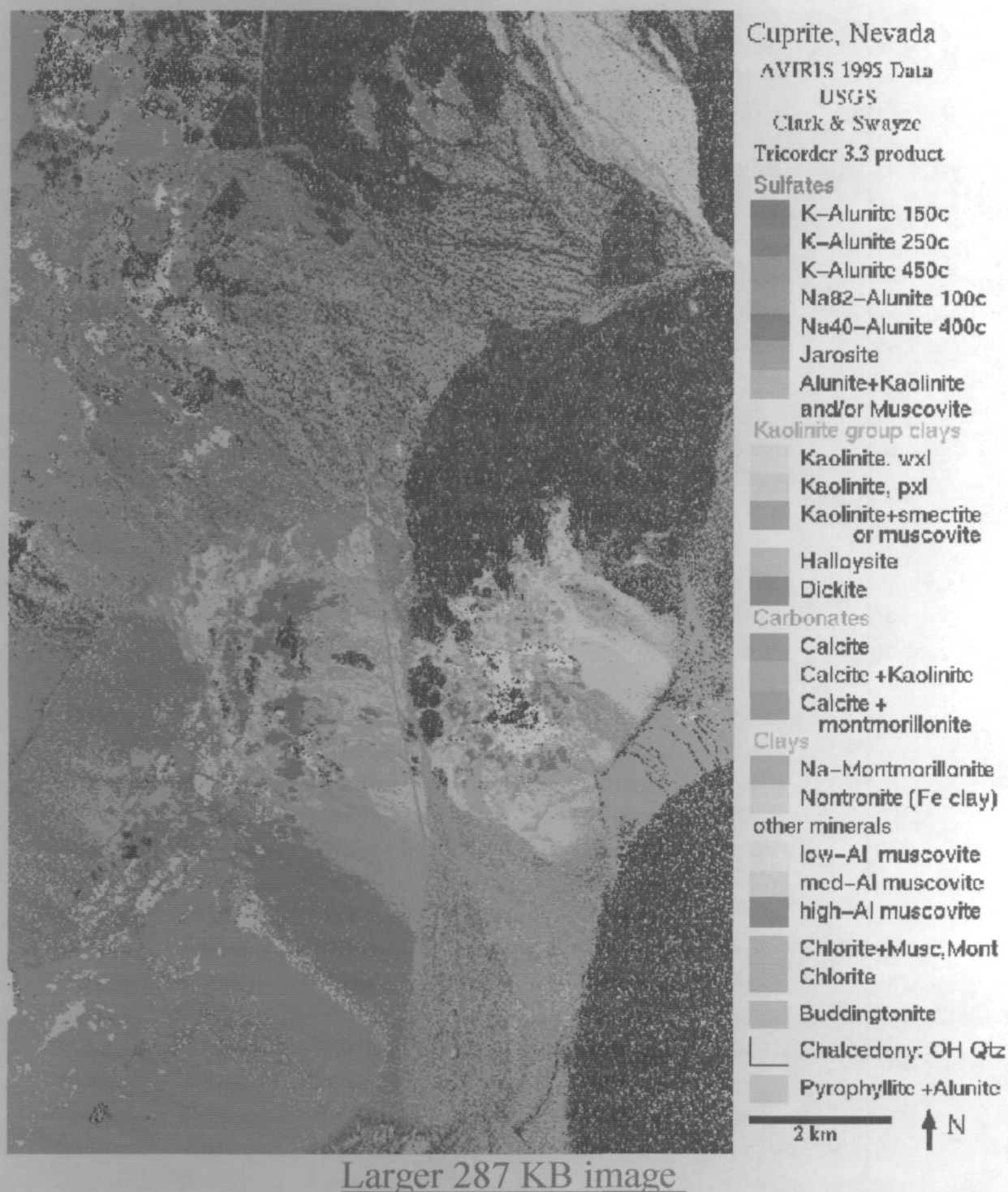
Randomly selected *small* samples could detect large or virtually no richterite (see flake variability in Figure 12). Even with sample preparation that includes liquids to clean a larger sample, richterite could still adhere to the vermiculite. Thus, detection in any environment can be inconsistent unless sampling can be done on a large sample volume, probing the sample undisturbed and unprocessed, like that which can be probed rapidly with tools like reflectance spectroscopy. Yet to be understood is how/if the richterite fibers can be released to become airborne. What electrostatic/mechanical/humidity/other conditions will permit that release?





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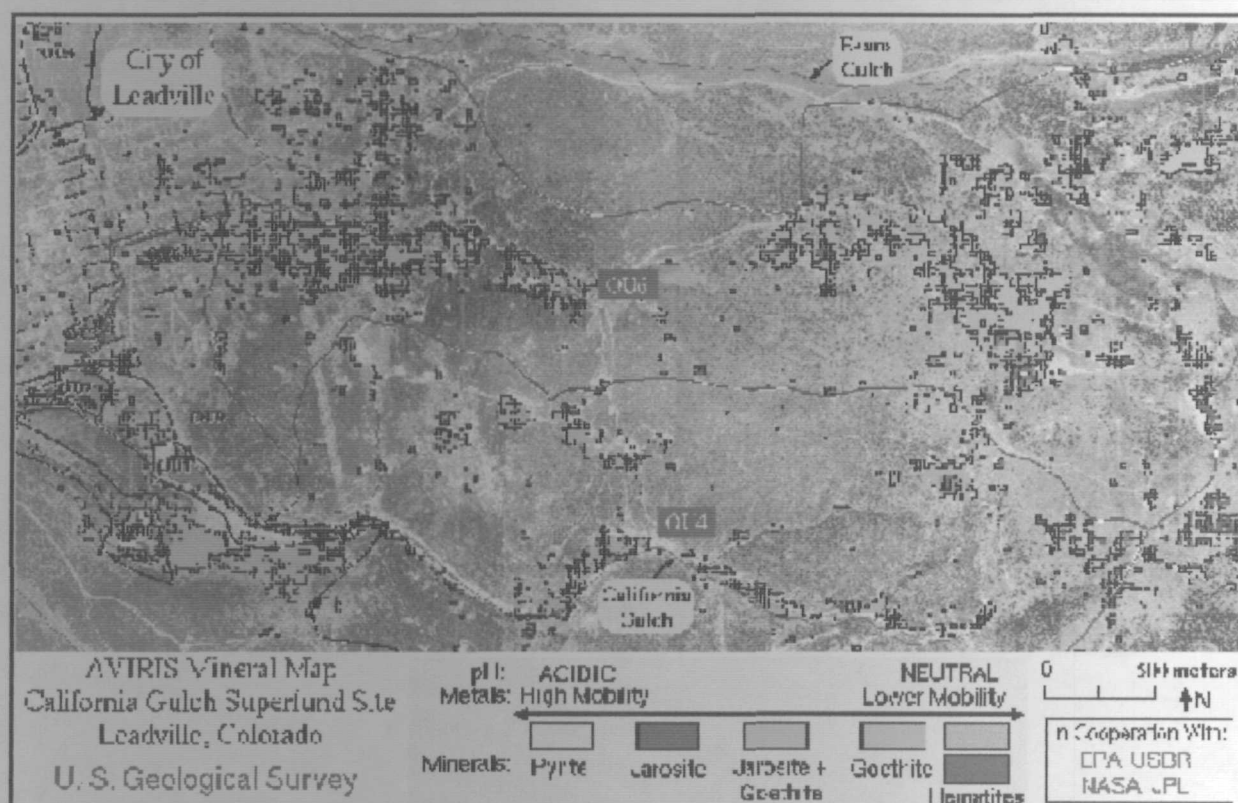
Figure 16. Reflectance Imaging Spectroscopy has developed into a spectacular new tool over the last decade for detecting and mapping chemistry, including solids (like minerals), liquids, and gases. Here is a mineral map of the Cuprite, Nevada area showing minerals exposed in two hydrothermal alteration systems. Many tens of minerals were mapped with imaging spectroscopy, a few of which are shown here. ground resolution is 17 meters, but the instrument can be flown at lower altitudes giving higher spatial resolution.



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Figure 17. Continuation of minerals mapped at Cuprite from Figure 17. AVIRIS data over this ~180 square km area was obtained in about 1.5 minutes. Other maps (not shown) show vegetation distribution, as well as other minerals. You can see more images of this and other areas on our web site at

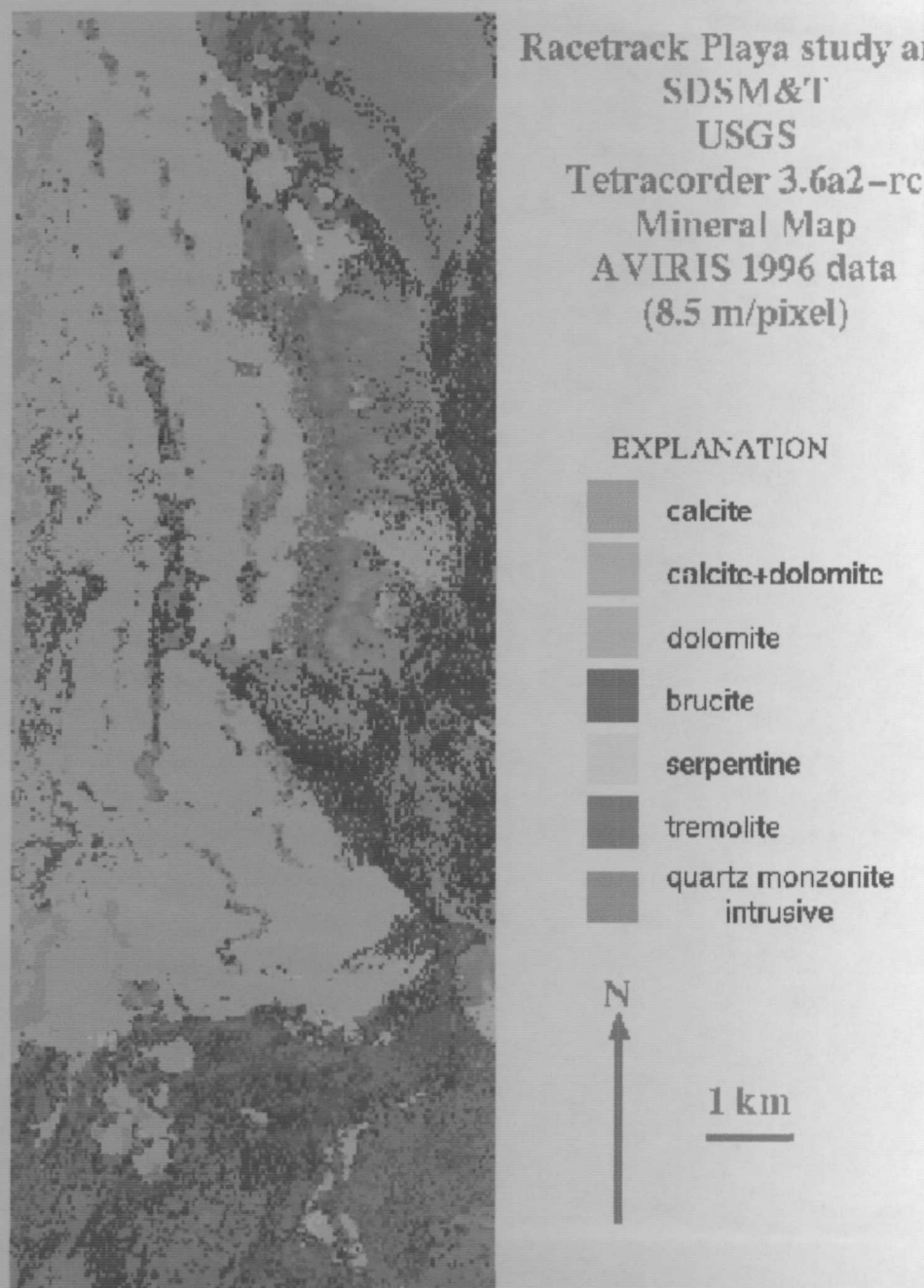
<http://speclab.cr.usgs.gov>. There are also maps at a couple of meter spatial resolution showing more minerals in fine detail not seen here.



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Figure 18. A third example of imaging spectroscopy mapping was our mapping of acid-generating mineralogy at Leadville, Colorado.

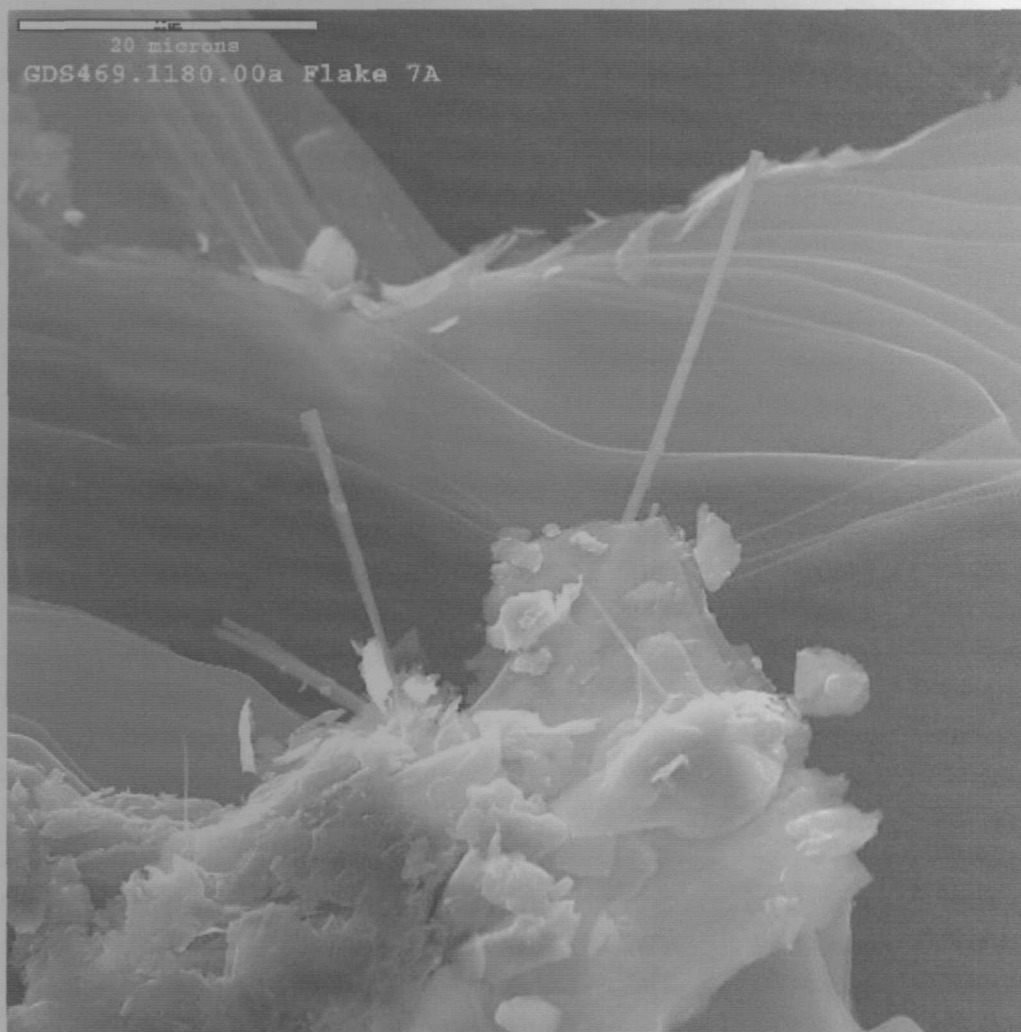
This resulting map shows source locations of acid-generating minerals, accelerating the cleanup by about 2 years and saving about \$2.5 million. Similar mapping in the Libby region could be used as guides to help remediation.



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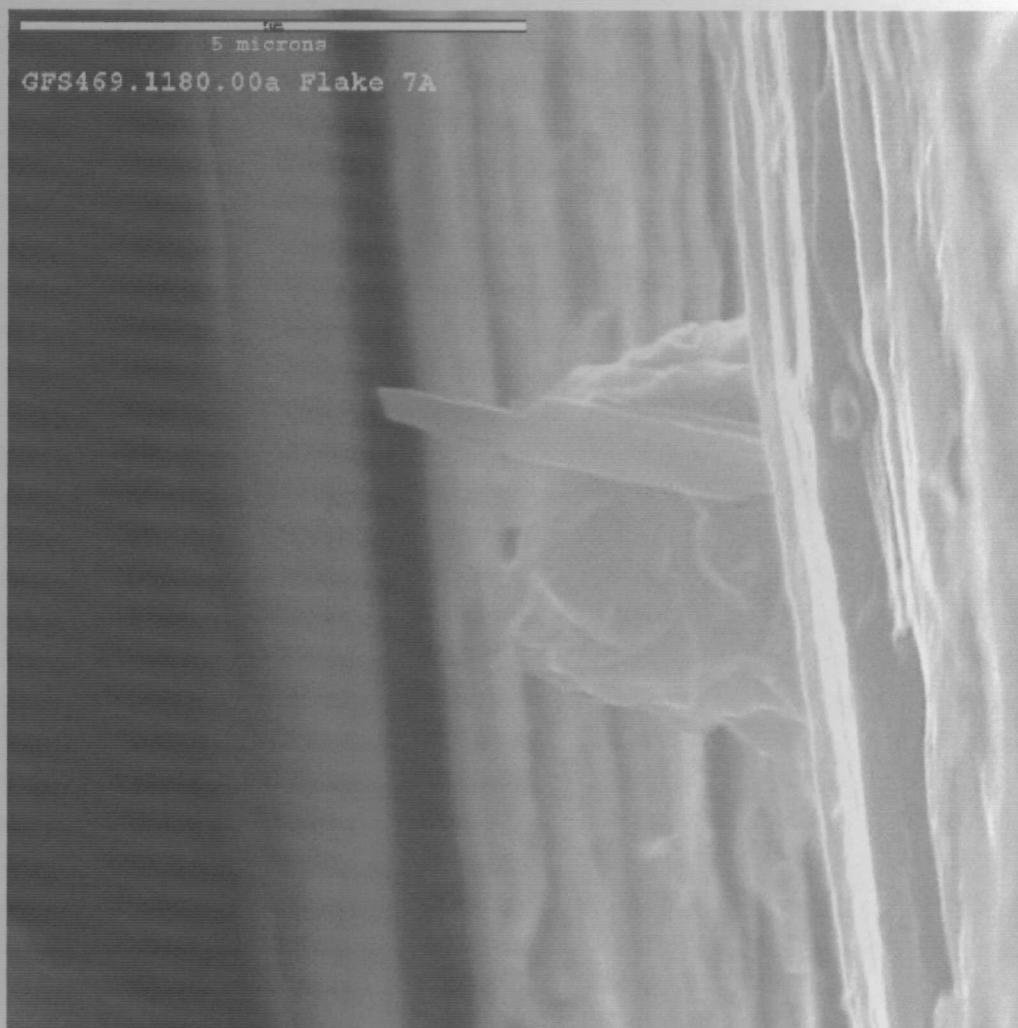
Figure 19. Imaging spectroscopy mapping in the Death Valley region by Ed Duke and colleagues (South Dakota School of Mining and Technology, and the USGS) show that asbestiform minerals can be mapped with this technology. Here, serpentine (chrysotile) in yellow, and tremolite in magenta are shown in small outcrops. Image is 8.5 meters/pixel sampling but pixel size

is 17 meters.



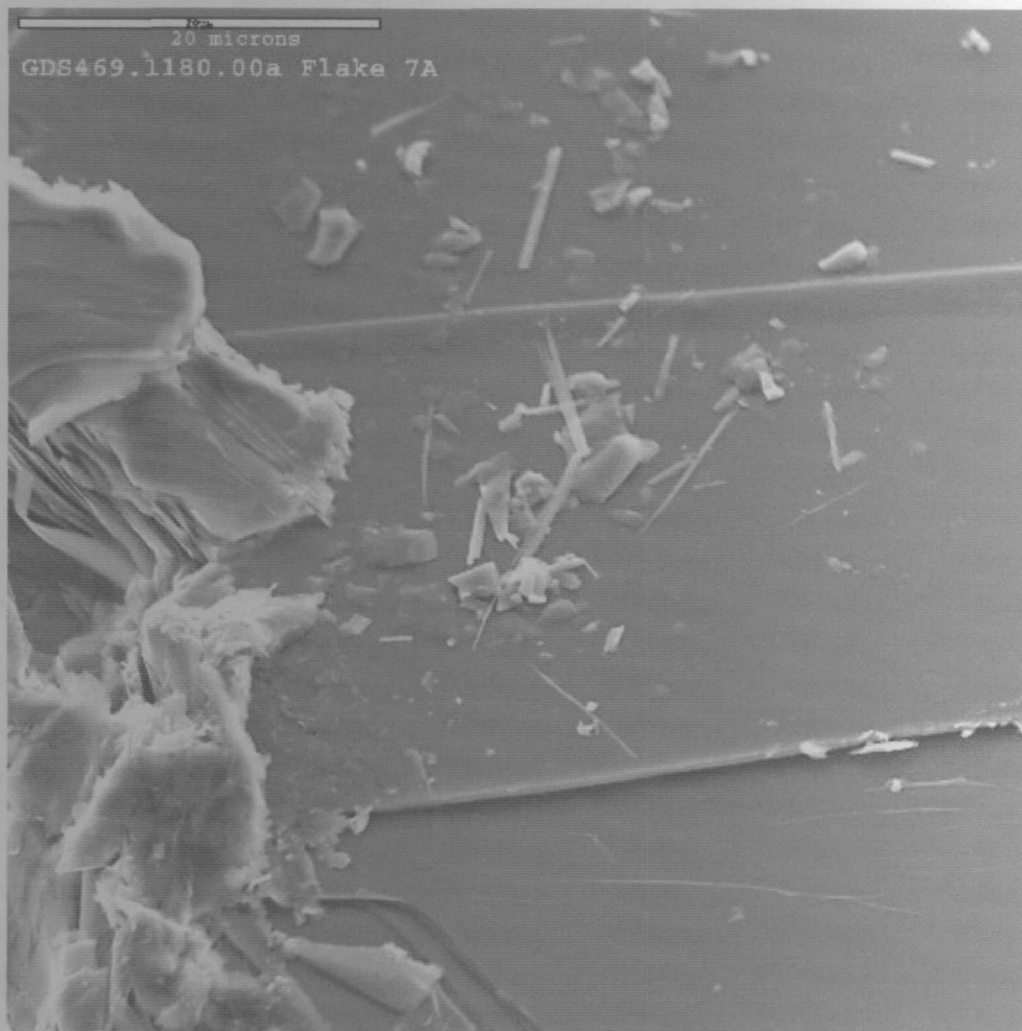
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Figure 20. SEM image of a split portion of flake 7 (see Figure 12), called flake 7a, shows richterite fibers sticking out of the edge of the flake. Are the fibers embedded in the vermiculite, or were they electrostatically adhering to the surface of the (19 times) ultrasonically washed flake and became embedded in the side during splitting of the flake?



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Figure 21. Another image of flake 7a showing a richterite in the side of the vermiculite fibers. Again, did this fiber get embedded in the side during sample handling or is the richterite embedded between the vermiculite layers?



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Figure 22. Another SEM image of flake 7a, this one showing richterite fibers on the surface. Other SEM images show embedded fiber-looking structures but their composition is unknown. One fiber found sticking up out of the vermiculite was high iron content and not an amphibole. Further study needs to be done to understand if richterite exists within the vermiculite flakes or if our observations are surface effects only. This is an important question as embedded fibers could represent continual generation of fibers into the air if the vermiculite grains were mechanically broken, as they might be on a dirt road with cars and trucks crushing the flakes.

Visible-Near IR Reflectance Spectroscopy Costs

- **Aircraft: NASA AVIRIS** system highest quality (Thus highest sensitivity)
 - **1 flight:** approximately **22 million samples** (spectra of points on the ground)
 - Flight cost: \$44k for low altitude \$95k for high altitude.
 - Analysis cost: \$100 to 300K depends on site characteristics.
 - Example: low altitude + \$200k analysis:
 $\$244,000 / 22,000,000 = 1.1 \text{ cents/sample!}$
- **Lab/Field spectroscopy** analysis:
 - Small quantities (tens to hundreds) less than \$30/sample (Not including per diem for field crew, (cost limited by documentation time, not data acquisition time.)
 - Large field spectroscopy sampling (like grid surveys) could be much less than the above, perhaps less than a few dollars /spot.
 - (Time in the field depends on weather.)

Conclusions / Discussion

The mineralogic properties of the Libby, MT ore body shows unusual electrostatic properties, and large variability in richterite concentration in laboratory samples, even in washed and well mixed vermiculite-biotite samples. This variability could pose difficulty in getting consistent analysis results concerning richterite content.

We propose a two-phased approach to detect and characterize Libby amphiboles (will work at other sites and mineral types too).

- 1) Screening with:
 - **Visible-NIR Reflectance Spectroscopy (VNIRRS: 0.4-2.5 microns):**
 - from aircraft to locate areas of greatest concentration,
 - in the field to screen which samples might be collected,
 - in the lab screening collected samples.
 - 2) On selected high (and low) amphibole-containing samples as indicated by spectroscopy, confirm asbestiform fibers with a method such as **SEM**.
 - 3) Selected samples should also be screened with **XRD** to confirm presence/absence of other minerals which might limit

spectroscopy sensitivities, and to confirm spectroscopy sensitivity.

U.S. Geological Survey, a bureau of the U.S. Department of the Interior

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